

Luminescence dynamics of a photosensitizer in a photocatalytic model system

S. Göde, Institute of Physics, University of Rostock, Germany (August 2010)



Application Note

Introduction

The photocatalytic cleavage of water using visible light for hydrogen generation attracts high attention. The aim is to develop an efficient method to use solar energy to transform water into a sustainable hydrogen fuel. Here, we study the hydrogen generation process for a homogeneous, photocatalytic active model system consisting of a catalyst (cat), an organo-metallic photosensitizer (PS) and a sacrificial reductant (SR) that substitutes the oxygen generation process (see Figure 1).

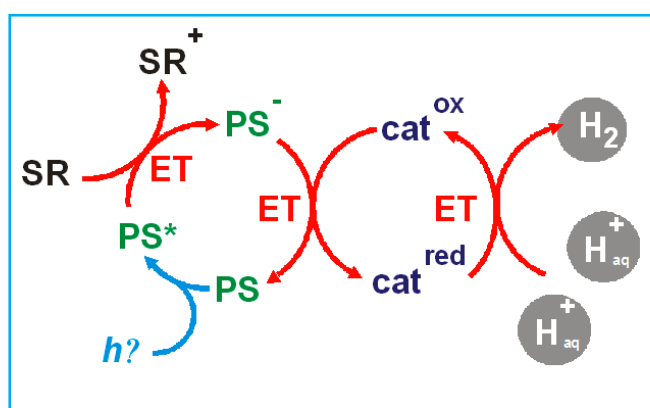


Figure 1: Reaction scheme for the water reduction cascade by electron transfer (ET) processes with a photosensitizer (PS), a catalyst (cat), and a sacrificial reductant (SR).[1]

Due to the manifold of participating species the involved processes are complex and little is known about the mechanisms and dynamics of the individual reaction steps within this electron transfer (ET) cascade.

Experiment

In a first step we concentrate on the initial reaction channel, that is the photoluminescence of PS in THF solution after fs-laser excitation ($\lambda = 400$ nm). The measurements are performed in a standard 1 cm fluorescence cuvette. The emitted light is detected perpendicular with respect to the incoming laser beam by a spectrograph (Andor Shamrock SR-303i-B) combined with an intensified CCD camera (Andor iStar DH740i-18U-05), see Fig. 2.

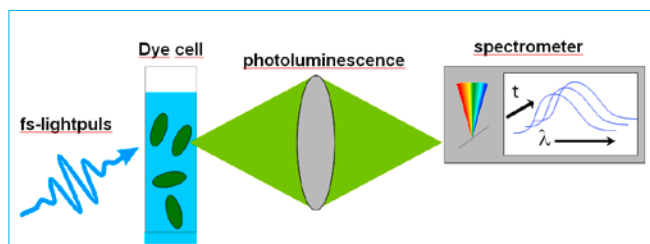


Figure 2: Principle of the nanosecond-resolved photoluminescence measurements.

The photoluminescence spectrum of PS is shown in Figure 3.

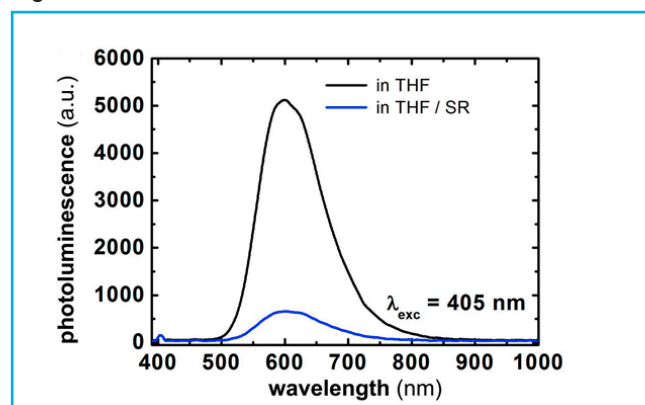


Figure 3: Steady-state photoluminescence spectra of the photosensitizer (PS) in pure tetrahydrofuran (THF) and in a THF/SR mixture. Although the spectrum remains unchanged in the spectral distribution the additional sacrificial reductant (SR) strongly reduces the photoluminescence yield.

The maximum of the broad emission band peaks at about 600 nm. When adding SR to the solution the fluorescence spectrum qualitatively remains unchanged, indicating that formation of new luminescent species did not occur. However, the signal of the PS is strongly quenched in the presence of the SR, which can be attributed to the appearance of an additional reaction channel namely the electron transfer process between the photoexcited state of the photosensitizer PS* and the SR.

In order to gain more insight into the dynamics of this process the time-resolved photoluminescence was measured using the gate-function of the camera. Due to the short lifetime of the excited state of PS the ultrafast gate modus with a gate width of 2 ns was applied. This short optical gate was shifted with respect to the incoming laser pulse. For each time step the spectrum was measured and analyzed. The total photoluminescence signal as a function of the time delay is shown in Figure 4 for both solutions.



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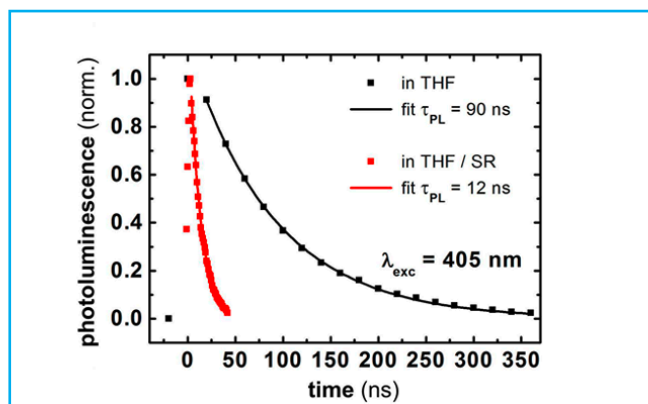


Figure 4: Decay of the photoluminescence signal of the photosensitizer (PS) in pure THF and in a THF / SR mixture and their exponential fitting curves. Adding SR the lifetime decreases by a factor of ten indicating that electron transfer takes place.

From the monoexponential decay one can determine the lifetimes of the luminescent electronic state. In the presence of SR the measured lifetime decreases from 90 ns to 12 ns in accordance with the lower photoluminescence quantum yield.

In future work, the studies will be extended by adding the catalyst to gain insight into the dynamics of the electron transfer processes for the active photocatalytic system.

Conclusion

The Andor system consisting of a spectrograph combined with an intensified CCD-camera has proved to be a powerful system especially for weak, pulsed light signals.

References

- [1] Tinker, L. L.; McDaniel, N. D.; Bernhard, S. J. Mater. Chem. 2009, 19, 3328.

Contact

Sebastian Göde
Workgroup Clusters & Nanostructures
Institute of Physics
University of Rostock
Universitätsplatz 3
18055 Rostock
Germany

Phone: +49 381 498-6805

E-mail: sebastian.goede@uni-rostock.de

Web: web.physik.uni-rostock.de/cluster/